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IN THE UNITED STATES PATENT & TRADEMARK OFFICE

N RE APPLICATION OF	:
SATOSHI NIIYAMA, ET AL.	: EXAMINER: SADULA, J.
SERIAL NO: 09/807,425	:
FILED: JULY 3, 2001	: GROUP ART UNIT: 1756

FOR: LIQUID CRYSTAL OPTICAL ELEMENT AND METHOD FOR ITS PRODUCTION

LETTER TO EXAMINER

COMMISSIONER FOR PATENTS
ALEXANDRIA, VIRGINIA 22313

SIR:

As noted in the Amendment and Request for Reconsideration filed with the U.S. Patent and Trademark Office on October 3, 2003, Applicants submit herewith certified English translations of three priority documents (JP10/298620; 10/298621; and 10/298624 each filed on November 20, 1998) in this case. Applicants submission of certified English translations of the priority documents serves to perfect Applicants' claim to priority and antedate one or more references applied by the Examiner as prior art in the examination of the above-identified application.

Respectfully submitted,

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DECLARATION

COMMISSIONER FOR PATENTS

ALEXANDRIA, VIRGINIA 22313

SIR:

Now comes MASAYUKI KUWANO who deposes and says:

That my name is MASAYUKI KUWANO ;

That my address is 5-24-310, 3-chome, Nakamachi, Musashino-shi, Tokyo, Japan;

That I know well both the English and Japanese languages;

That the attached English language translation is true and correct translation of Japanese Patent Application No JP10-298620 filed on October 20, 1998 to the best of my knowledge and belief.

I hereby declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

FURTHER DEPONENT SAITH NOT.

October 3, 2003
Date

Masayuki Kuwano
MASAYUKI KUWANO

AB-126-PCT
(F99-95)
1/3

Date of Application: October 20, 1998

Application Number: Patent Application JP10/298620

Applicant: Asahi Glass Company, Limited

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【Reference No.】 980650

【Filing Date】 October 20, 1998

【Addressee】 Commissioner, Patent Office

【International Patent Classification】 G02F 1/13
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G02F 1/1335

【Title of the Invention】

LIQUID CRYSTAL OPTICAL ELEMENT AND METHOD FOR ITS PRODUCTION

【Number of Inventions Stated in Claim(s)】 7

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【Name of item】 Specification 1

【Name of item】 Abstract 1

【Burden of Proof】 Yes

【TYPE OF DOCUMENT】 SPECIFICATION

【TITLE OF THE INVENTION】

LIQUID CRYSTAL OPTICAL ELEMENT AND METHOD FOR ITS PRODUCTION

【SCOPE OF THE CLAIM(S)】

【Claim 1】

A method for producing a liquid crystal optical element, which comprises sandwiching a mixture of a liquid crystal with an uncured curable compound between a pair of substrates which are provided with transparent electrodes and of which at least one is transparent, and curing the curable compound to form a liquid crystal/cured composite layer, wherein the curable compound contains two types of curable compounds, of which the molecular weights are different by at least two times.

【Claim 2】

The method for producing a liquid crystal optical element according to Claim 1, wherein the curable compound contains a compound of the formula (1):

【Ka 1】

$A_1-(OR_1)_n-O-Z-O-(R_2O)_m-A_2$ Formula (1)

wherein each of A_1 and A_2 which are independent of each other, is an acryloyl group, a methacryloyl group, a glycidyl group or an allyl group; each of R_1 and R_2 which

are independent of each other, is a C_{2-6} alkylene group; Z is a bivalent mesogen structure; and each of n and m which are independent of each other, is an integer of from 1 to 10.

【Claim 3】

The method for producing a liquid crystal optical element according to Claim 1 or 2, wherein the curable compound contains a curable compound containing a mesogen structural portion in its molecule and a curable compound containing no mesogen structural portion.

【Claim 4】

The method for producing a liquid crystal optical element according to Claim 1, 2 or 3, wherein the two types of curable compounds have curable sites connectable to each other.

【Claim 5】

The method for producing a liquid crystal optical element according to Claim 1, 2, 3 or 4, which contains a curable compound having a molecular weight of at least 1,000.

【Claim 6】

The method for producing a liquid crystal optical element according to Claim 1, 2, 3, 4 or 5, wherein the mixture contains a very small amount of a curing catalyst.

【Claim 7】

A liquid crystal optical element produced by the

method as defined in any one of Claims 1 to 6.

【DETAILED DESCRIPTION OF THE INVENTION】

【Technical Field to which the Invention Belongs】

The present invention relates to a liquid crystal optical element whereby the transmittance, scattering and reflection state of the element is controlled by application/non-application of an electric field and which is useful for e.g. a light-controlling element, a display element or an optical shutter.

【Prior Art】

A transmission/scattering type optical element has been proposed in which a liquid crystal and a transparent polymer are combined to form a difference in the refractive index between the polymer and the liquid crystal or in the interior of the liquid crystal (among microscopic regions). It is called, for example, a liquid crystal/polymer composite element, a liquid crystal/resin composite element or a dispersion type liquid crystal element. In principle, this element requires no polarizing plate, whereby the light absorption loss is small, and a high scattering performance can be obtained, and thus, it has a significant merit in that the light-utilizing efficiency in the entire element is high.

By utilizing such characteristics, it is employed for a light-controlling glass, an optical shutter, a laser apparatus and a display apparatus. One showing a

scattering state under application of no voltage and a transparent state under application of a voltage, has been commercialized.

Further, prior art reference 1 (USP 5,188,760) discloses an element employing a liquid crystal and a polymerizable liquid crystal. According to this prior art reference 1, under application of no voltage, the element shows a transparent state as observed from any direction as the liquid crystal and the polymerized liquid crystals in the element have the same alignment direction, and under application of a voltage, the alignment of the liquid crystals in the element is controlled by an electric field, and the alignment direction of liquid crystal molecules changes variously in the microscopic regions, whereby the element shows a scattering state.

Further, it has been disclosed that the contrast ratio can be improved by adding a chiral agent to provide a helical structure in the initial alignment. This element is called "an anisotropic gel" or "a liquid crystal gel". In this prior art reference 1, a mesogen monomer having acryloyl groups at the terminals was used.

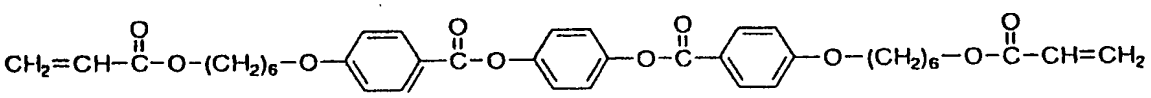
Further, prior art reference 2 (PCT International Publication WO92/19695) also discloses an element having a similar structure. The operation mode was the same as in prior art reference 1, and a very small amount of a polymer is dispersed in the chiral nematic liquid crystal

to obtain a transparent state under application of no voltage and a scattering state under application of a voltage. This element is called PSCT (polymer stabilized cholesteric texture). Also in this prior art reference 2, a mesogen monomer having acryloyl groups at the terminals, was disclosed.

【Problems that the Invention is to Solve】

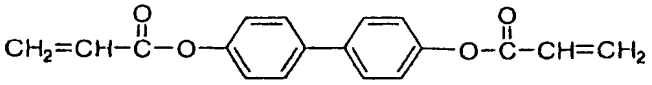
As the structures of uncured curable compounds, prior art reference 1 has disclosed the compound of the formula (2), and the prior art reference 2 has disclosed the compound of the formula (3);

【Ka 2】



Formula (2)

【Ka 3】



Formula (3)

However, the cured products formed by using these compounds alone had characteristics attributable to the molecular structures. Namely, a highly crystallizable rigid mesogen portion is contained and the distance between the curable sites (acryloyl groups in this case) is short, and accordingly, the molecular weight between the crosslinking points tends to be small, whereby the obtained cured products tend to be hard and brittle.

Further, for the same reason, the mobility of the uncured sites during the curing will be substantially impaired, whereby there has been a problem that a long curing time is required for adequate curing.

Characteristics of a liquid crystal optical device obtained by curing the curable compound in the mixture, depend largely on the structure of the liquid crystal/cured composite layer. Further, its structure will give a substantial influence over the molecular structure of the uncured curable compound.

It has been reported that in general, with a curable compound containing a mesogen structure such as a biphenyl structure, curable sites at both ends will bond, the modulus of elasticity after being cured is large, and the glass transition temperature of the obtainable polymer is also high.

On the other hand, this means that restrictions are given to the free volume and the molecular motion of the curable compound during the curing, and at the later stage of the curing process, the reactivity of the curable sites is likely to be suppressed, and there has been a problem that the curing reaction tends to be not enough, or a very long curing time will be required.

Further, the physical properties of the resin as the cured product of the liquid crystal/cured composite layer, related to the electro-optical characteristics of the liquid crystal optical element. If the modulus of

elasticity of the resin was too high or too brittle, the required driving voltage tended to be high, and at a relatively low driving voltage range, no adequate contrast ratio in the reflectance change or in the transmittance change was sometimes obtained between application and non-application of a voltage.

It is an object of the present invention to solve the above problems and provide a liquid crystal optical element which can be produced, for example, in a short period of curing time and which has a high contrast ratio even at a low driving voltage.

【Means of Solving the Problems】

Namely, the present invention provides a method for producing a liquid crystal optical element, which comprises sandwiching a mixture of a liquid crystal with an uncured curable compound between a pair of substrates which are provided with transparent electrodes and of which at least one is transparent, and curing the curable compound to form a liquid crystal/cured composite layer, wherein the curable compound contains two types of curable compounds, of which the molecular weights are different by at least two times.

Further, the present invention also provides the production method for producing a liquid crystal optical element wherein the curable compound contains a compound of the following formula (1). In the above production method, three or more compounds having different

molecular weights may be employed, so long as at least two types of compounds among them satisfy the above-mentioned conditions.

【Ka 4】

$$A_1-(OR_1)_n-O-Z-O-(R_2O)_m-A_2 \quad \text{Formula (1)}$$

wherein each of A_1 and A_2 which are independent of each other, is an acryloyl group, a methacryloyl group, a glycidyl group or an allyl group; each of R_1 and R_2 which are independent of each other, is a C_{2-6} alkylene group; Z is a bivalent mesogen structure; and each of n and m which are independent of each other, is an integer of from 1 to 10.

【Mode of Carrying out the Invention】

In the present invention, the uncured curable compound contains two types of curable compounds, of which the molecular weights are different by at least two times, whereby the molecular weight between the crosslinking points of the resin during the curing process or after the curing may be changed. Or, the crystallinity of the resin may be controlled. The curing property in the curing process can be thus improved, and the modulus of elasticity of the resin after the curing can be adjusted, whereby it is possible to obtain a liquid crystal optical element which is capable of presenting a high contrast even at a low driving voltage.

Further, when the uncured curable compound contains a curable compound of the formula (1), the compatibility

with an uncured liquid crystal can be improved. Further, it has been found that by introducing an oxyalkylene structure having a high molecular mobility between the mesogen structural portion and the curable site, the molecular mobility at the curable site in the curing process can be improved, and it is possible to obtain a liquid crystal optical element which has a high reliability and a high contrast, even by a curing reaction for a short time, and wherein the state under application or non-application of an electric field, is stable.

The curable sites (A_1, A_2) of the formula (1) may be any of the above-mentioned functional groups which are photo curable or heat curable usually in the presence of a curing catalyst. Among them, an acryloyl group or a methacryloyl group suitable for photo curing, is preferred, since the temperature for the curing can be controlled.

The carbon numbers of the oxyalkylene portions R_1 and R_2 of the formula (1) are preferably from 2 to 6 from the viewpoint of the mobility. Further, an ethylene group having a carbon number of 2 and a propylene group having a carbon number of 3, are preferred.

As the mesogen structural portion (Z) of the formula (1), a bivalent polyphenylene having at least two 1,4-phenylene groups bonded, is preferred. Further, some of 1,4-phenylene groups in this polyphenylene group may be

bivalent organic groups substituted by a 1,4-cyclohexylene group.

Some or all of the hydrogen atoms of such a polyphenylene group or a bivalent organic group may be substituted by a substituent such as a C_{1-2} alkyl group, a halogen atom, a carboxyl group or an alkoxycarbonyl group. Preferred Z is a biphenylene group having two 1,4-phenylene groups bonded (hereinafter referred to as a 4,4'-biphenylene group), a terphenylene group having three such phenylene groups bonded, and a bivalent organic groups having from 1 to 4 hydrogen atoms of such a group substituted by a C_{1-2} alkyl group, a fluorine atom, a chlorine atom or a carboxyl group. Most preferred Z is a 4,4'-biphenylene group having no substituent.

If n and m of the formula (1) are too large, the compatibility with the liquid crystal deteriorates, and each of them is from 1 to 10, further preferably from 1 to 4 taking into consideration the characteristics of the element after curing.

In order to adjust the compatibility with the liquid crystal before the curing and the modulus of elasticity of the resin after the curing, it is preferred that the uncured curable compound contains a curable compound containing a mesogen structural portion in its molecule and a curable compound containing no such a structural portion. Because, the mesogen structural portion

improves the compatibility with the liquid crystal before the curing, while it tends to increase the modulus of elasticity of the resin after the curing more than necessary.

It is preferred that the contained two types of uncured curable compound can be bonded to each other, thereby to avoid phase separation of resins in the resin formed by curing and to avoid an increase of the haze at the time of reflection or transmission.

In order to lower the modulus of elasticity of the resin after curing by improving the curing property during the curing by increasing the molecular weight between the crosslinking points, it is preferred to employ a curable compound having a relatively large molecular weight as the uncured curable compound. Specifically, a curable compound having a molecular weight of at least 1000, is preferred.

The mixture of a liquid crystal with an uncured curable compound, may contain a curing catalyst, and in the case of photo curing, a photo polymerization initiator which is commonly used for a photo curable resin may be employed such as a benzoin ether type, an acetophenone type or a phosphine oxide type. In the case of thermosetting, a curing catalyst such as a peroxide type, a thiol type, an amine type or an acid anhydride type, may be used depending upon the type of the curable sites, and if necessary, a curing assistant such as an

amine may also be used.

The content of the curing catalyst is preferably at most 20 wt% of the uncured curable compound contained, and in a case where a high molecular weight or a high resistivity is required for the cured product after curing, it is more preferably from 1 to 10 wt%.

Further, in order to improve the contrast of the element between application and non-application of an electric field, a chiral agent may be added to the mixture of a liquid crystal with an uncured curable compound. The helical pitch thereby induced is preferably at least 5 μm and at most two times of the electrode gap, since if it is too small, the driving voltage will increase, and if it is too large, no adequate contrast will be obtained.

On the other hand, the mixture of a liquid crystal with an uncured curable compound, is preferably a homogeneous solution after mixing. Further, the mixture of a liquid crystal with an uncured curable compound may show a liquid crystal phase when sandwiched between the substrates provided with electrodes. The mixture of a liquid crystal with an uncured curable compound, may show a liquid crystal phase when it is cured.

It is also possible to impart a function to align the liquid crystal to the electrode surface by directly rubbing the electrode surface of the substrates provided with electrodes, which sandwich the mixture of a liquid

crystal with an uncured curable compound, or by forming a thin film of a resin thereof and rubbing the thin film, whereby it is possible to reduce irregularities at the time of sandwiching the mixture of a liquid crystal and an uncured curable compound.

Further, the combination of the alignment directions of the pair of alignment-treated substrates may be parallel or orthogonal, and the angle may be set to make the irregularities be minimum at the time of sandwiching the mixture.

The distance between the electrodes may be maintained by e.g. a spacer, and the gap is preferably from 4 to 50 μm, more preferably from 5 to 30 μm. If the electrode gap is too small, the contrast tends to deteriorate, and if it is too large, the driving voltage will increase.

The substrates supporting electrodes, may be glass substrates or resin substrates, or a combination of a glass substrate and a resin substrate. Further, one side may be a reflecting electrode made of an aluminum or dielectric multi-layer film.

In the case of film substrates, the productivity is high, because it is possible that continuously supplied substrates provided with electrodes, are sandwiched between pairs of rubber rolls, and a mixture of a liquid crystal and an uncured curable compound, having a spacer incorporated and dispersed therein, is sandwiched between

them, followed by continuous curing.

In the case of glass substrates, a very small amount of a spacer is distributed inside of the electrode surfaces, and the four sides of the opposing substrates are sealed with a sealing agent such as an epoxy resin to form a sealed cell, and one of cutouts of the seal formed at two or more portions is dipped in a mixture of a liquid crystal with an uncured curable compound, and suctioning from the other to fill the mixture into the cell, followed by curing to obtain a liquid crystal optical element. Otherwise, a vacuum injection method may also be employed. Now, the present invention will be described in detail with reference to examples.

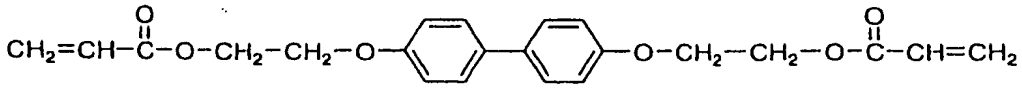
【Mode of Carrying out the Invention】

【Examples】

EXAMPLE 1

A mixture (mixture A) having 94.6 parts of a cyano type nematic liquid crystal (BL-009, manufactured by Merck), 2.4 parts of a chiral agent (a mixture of S-811, manufactured by Merck and C15 manufactured by Merck in a weight ratio of 1:1), 2.5 parts of a curable compound of the formula (4) having a molecular weight of 382, 0.5 part of a urethane acrylate oligomer (EB-270, manufactured by UCB) having a molecular weight of at least 1500 and 0.09 part of benzoin isopropyl ether, was prepared.

【Ka 5】



Formula (4)

This mixture A was injected into a liquid crystal cell prepared by bonding a pair of substrates having thin polyimide films formed on transparent electrodes and rubbed in one direction, so that the rubbing directions crossed each other, via a very small amount of resin beads having a diameter of 13 μm, by an epoxy resin printed in a width of about 1 mm along the four sides.

While maintaining this liquid crystal cell at 25°C, ultraviolet rays of 3 mW/cm^2 from the upper side and ultraviolet rays of about 3 mW/cm^2 from the lower side, were irradiated for 10 minutes by a HgXe lamp having a main wavelength of about 365 nm, to prepare a liquid crystal optical element.

An operation of applying a voltage of 20 Vrms with a rectangular wave of 50 Hz to this liquid crystal optical element for 10 minutes and then removing the voltage, was repeated ten times. Then, the transmittance was measured by a transmittance measuring system (F value of the optical system: 11.5) employing a measuring light source having a center wavelength of 530 nm and a full width at half maximum value of about 20 nm, whereby the transmittance was 83% when no voltage was applied, and

the value of a contrast ratio obtained by dividing this value by the transmittance when 20 Vrms was applied, was 31.

COMPARATIVE EXAMPLE 1

A liquid crystal optical element was obtained in the same manner as in Example 1 except that only the compound of the formula (4) was used as the uncured curable compound. To this liquid crystal optical element, the voltage was applied in the same manner as in Example 1, and the transmittance was measured by the same measuring system, whereby the transmittance was 83% when no voltage was applied, and the value of a contrast ratio obtained by dividing this value by the transmittance when 20 Vrms was applied, was 11.

EXAMPLE 2

Mixture A prepared in Example 1 was injected into the same liquid crystal cell as in Example 1, and while maintaining it at 25°C, ultraviolet rays were irradiated for 3 minutes in the same manner as in Example 1 to obtain a liquid crystal optical element.

An operation of applying a voltage of 20 Vrms with a rectangular wave of 50 Hz to this liquid crystal optical element for 10 minutes and then removing the voltage, was repeated ten times. Then, the transmittance was measured by a transmittance measuring system (F value of the optical system: 11.5) employing a measuring light source having a center wavelength of 530 nm and a full width at

half maximum value of about 20 nm, whereby the transmittance was 79% when no voltage was applied, and the value of a contrast ratio obtained by dividing this value by the transmittance when 20 Vrms was applied, was 43.

COMPARATIVE EXAMPLE 2

A liquid crystal optical element was obtained in the same manner as in Example 2 except that only the compound of the formula (2) was used as the uncured curable compound.

To this liquid crystal optical element, the voltage was applied in the same manner as in Example 2, and the transmittance was measured by the same measuring system, whereby the transmittance was 81% when no voltage was applied, and the value of a contrast ratio obtained by dividing this value by the transmittance when 20 Vrms was applied, was 12.

【Effects of the Invention】

Since the curing property of the curable compound used for the liquid crystal optical element of the present invention is high, and it is possible to prepare a liquid crystal optical element having a high contrast in the transmittance or reflectance between application and non-application of an electric field, in a short period of curing time, whereby the productivity is high.

Further, the modulus of elasticity or the molecular weight between crosslinking points of the cured resin can

be controlled, whereby a liquid crystal optical element showing a high contrast ratio, can be obtained even at a low driving voltage, and is suitable for e.g. displays, optical shutters and light-controlling glasses for which driving voltage is limited.

【TYPE OF DOCUMENT】 ABSTRACT

【SUMMARY】

【OBJECT】

It is an object to obtain a liquid crystal optical element which is operable at a low driving voltage and has a high contrast ratio.

【MEANS OF SOLVING PROBLEMS】

A method for producing a liquid crystal optical element, which comprises sandwiching a mixture of a liquid crystal with an uncured curable compound between a pair of substrates which are provided with transparent electrodes and of which at least one is transparent, and curing the curable compound to form a liquid crystal/cured composite layer, wherein the curable compound contains two types of curable compounds, of which the molecular weights are different by at least two times.

【SELECTED FIGURE】 No Selected Figure